and makes it possible to form a metal-film-buried pattern having a high reliability with a good productivity, workability and yield.

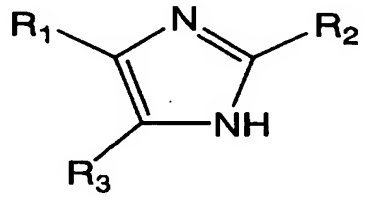
DISCLOSURE OF THE INVENTION

The polishing slurry of the present invention relates to a polishing slurry for metal and a polishing method according to the following (1) to (18):

(1) A polishing slurry for metal, comprising an oxidizer, a metal oxide dissolving agent, a metal inhibitor, and water, wherein the metal inhibitor comprises:

a compound having an amino-triazole skeleton wherein an amino group is bonded to carbon in a triazole ring; and

a compound having an imidazole skeleton and represented by the following general formula (I):



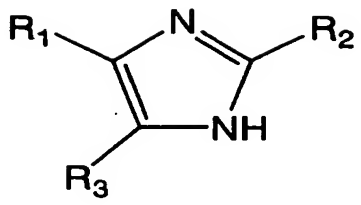
(I)

wherein R_1, R_2 and R_3 each independently represent a hydrogen atom, an amino group, or a C_1-C_{12} alkyl chain provided that the case that all of R_1, R_2 and R_3 are hydrogen atoms is excluded.

(2) A polishing slurry for metal, comprising an oxidizer, a metal oxide dissolving agent, a metal inhibitor, and water, wherein the metal inhibitor comprises:

a compound having a triazole skeleton having no amino group; and

a compound having an imidazole skeleton and represented by the following general formula (I):



(I)

wherein R_1, R_2 and R_3 each independently represent a hydrogen atom, an amino group, or a C_1-C_{12} alkyl chain provided that the case that all of R_1, R_2 and R_3 are hydrogen atoms is excluded.

(3) A polishing slurry for metal, comprising an oxidizer, a metal oxide dissolving agent, a metal inhibitor, and water, wherein the metal inhibitor comprises:

a compound having an amino-triazole skeleton wherein an amino group is bonded to carbon in a triazole ring; and

a compound having a triazole skeleton having no amino group.

(4) The polishing slurry according to the above-mentioned (1) or (3), wherein the compound having the amino-triazole skeleton is 3-amino-1,2,4-triazole.

(5) The polishing slurry according to the above-mentioned (1) or (2), wherein the compound having the imidazole skeleton is at least one selected from the group consisting of 2-methylimidazole, 2-ethylimidazole, 2-(isopropyl)imidazole, 2-propylimidazole, 2-butylimidazole, 4-methylimidazole, 2,4-dimethylimidazole, and 2-ethyl-4-methylimidazole.

(6) The polishing slurry according to the above-mentioned (2) or (3), wherein the compound having the triazole skeleton having no amino group is at least one selected from the group consisting of 1,2,3-triazole, 1,2,4-triazole, benzotriazole, and 1-hydroxybenzotriazole.

(7) The polishing slurry according to any one of the

above-mentioned (1) to (6), wherein the metal inhibitor comprises the compound having the amino-triazole skeleton, the compound having the triazole skeleton having no amino group, and the compound having the imidazole skeleton.

(8) The polishing slurry for metal according to any one of the above-mentioned (1) to (7), further comprising a water-soluble polymer.

(9) The polishing slurry for metal according to the above-mentioned (8), wherein the water-soluble polymer is at least one selected from polysaccharides, polycarboxylic acids, polycarboxylic acid esters, polycarboxylic acid salts, polyacrylamide, and vinyl polymers.

(10) The polishing slurry for metal according to any one of the above-mentioned (1) to (9), wherein the oxidizer for metal is at least one selected from the group consisting of hydrogen peroxide, nitric acid, potassium periodate, hypochlorous acid, persulfates, and ozone water.

(11) The polishing slurry for metal according to any one of the above-mentioned (1) to (10), wherein the metal oxide dissolving agent is at least one selected from the group consisting of organic acids, organic acid esters, ammonium salts of organic acids, and sulfuric acid.

(12) The polishing slurry for metal according to any one of the above-mentioned (1) to (11), further comprising an abrasive.

(13) The polishing slurry for metal according to any one of the above-mentioned (1) to (12), wherein a metal film to be polished is at least one selected from the group consisting of copper, copper alloys, copper oxides, oxides of copper alloys,

tantalum and compounds thereof, titanium and compounds thereof, and tungsten and compounds thereof.

(14) A method for polishing a metal film by supplying the polishing slurry for metal according to any one of the above-mentioned (1) to (13) onto a polishing cloth of a polishing table while moving the polishing table and a substrate having the metal film relatively in the state that the substrate is pressed against the polishing cloth.

(15) The polishing method according to the above-mentioned (14), wherein the metal film is at least one selected from the group consisting of copper, copper alloys, copper oxides, oxides of copper alloys, tantalum and compounds thereof, titanium and compounds thereof, and tungsten and compounds thereof.

(16) The polishing method according to the above-mentioned (14) or (15), wherein a laminate of two or more metal films is continuously polished.

(17) The polishing method according to the above-mentioned (16), wherein a first film which is first polished among the two or more metal laminated films is one or more selected from copper, copper alloys, copper oxides, and oxides of copper alloys, and a second film which is next polished among them is one or more selected from tantalum and compounds thereof, titanium and compounds thereof, and tungsten and compounds thereof.

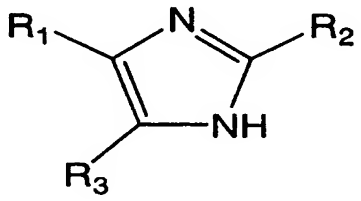
(18) A polishing method, comprising a first polishing step of polishing a wiring metal layer of a substrate, the substrate comprising an interlayer insulating film which has a surface consisting of concave portions and convex portions, a barrier layer which covers the interlayer insulating film along the surface

thereof, and a wiring metal layer which fills the concave portions to cover the barrier layer, and thereby making the barrier layer at the convex portions exposed, and a second polishing step of polishing at least the barrier layer and the wiring metal layer at the concave portions after the first polishing step, thereby making the interlayer insulating layer at the convex portions exposed, wherein the polishing is performed by use of the polishing slurry for metal according to any one of the above-mentioned (1) to (13) at least in the second polishing step.

BEST MODES FOR CARRYING OUT THE INVENTION

The present invention will be described in detail hereinafter.

The polishing slurry for metal of the invention comprises, as main constituent components, an oxidizer, a metal oxide dissolving agent, a metal inhibitor, and water. The metal inhibitor comprises a compound (A) having an amino-triazole skeleton wherein an amino group is bonded to carbon in a triazole ring and a compound (B) having an imidazole skeleton and represented by the following general formula (I):



(I)

wherein R_1, R_2 and R_3 each independently represent a hydrogen atom, an amino group, or a C_1-C_{12} alkyl chain provided that the case that all of R_1, R_2 and R_3 are hydrogen atoms is excluded; or comprises the compound (B) and a compound(C) having a triazole

skeleton having no amino group; or

comprises the compound (A) and the compound(C).

The present invention will be described by way of the following examples. The invention is not limited by these examples.

[Examples 1 to 4,6 to11, Reference Examples 1 and 2 and Comparative Examples 1 and 2]

(Method for producing polishing slurries for metal)

Polishing slurries for metal were each prepared by mixing: 0.15% by weight of malic acid; 0.15% by weight of a water-soluble polymer (an acrylic polymer, weight-average molecular weight: about 10000); 0.2% by weight of an aminotriazole compound shown in Table 1 or 2; 0.2% by weight of a benzotriazole shown in Table 1 or 2 and/or 0.05% by weight of an imidazole compound shown therein as one or more metal inhibitors other than the aminotriazole compound; 9% by weight of hydrogen peroxide; and water as the balance; the ratio of each of these being a ratio thereof to the total amount.

The resultant polishing slurries for metal were each used to perform etching and CMP polishing under conditions described below and then make evaluation. Table 1 shows each polishing speed in the CMP for a copper substrate and each etching speed thereto together, and Table 2 shows each polishing speed for a tungsten substrate and each etching speed thereto together.

(Polishing conditions)

Copper substrate: a silicon substrate on which metal copper of 1500 nm thickness was deposited

Tungsten substrate: a silicon substrate on which a tungsten compound of 600 nm thickness was deposited

Polishing slurry supplying amount: 15 cc/minute

Polishing pad: foamed polyurethane resin (model number: IC1000, manufactured by Rodel)

Polishing pressure: 29.4 kPa (300 gf/cm^2)

Relative speed between the substrate and the polishing table: 45 m/minute, and polishing table rotating speed: 75 rpm

(Items for evaluation)

Polishing speed: the difference between the film thicknesses of each of the films before and after the polishing was obtained by the conversion of the electric resistance values thereof.

Etching speed: each of the substrates was immersed into each of the polishing slurries for metal which were stirred (room temperature, 25°C, stirring: 600 rpm), and the difference between the film thicknesses of each of the metal layers before and after the immersing was obtained by the conversion of the electric resistance values thereof.

[Examples 13 to 20, Reference Examples 3 to 6, and Comparative Example 3]

(Method for producing polishing slurries for metal)

Polishing slurries for metal were each prepared by mixing: 0.15% by weight of malic acid; 0.15% by weight of a water-soluble polymer (an acrylic polymer, weight-average molecular weight: about 10000); 0.2% by weight of an imidazole compound shown in Table 3; 0.2% by weight of a benzotriazole or 3-amino-1,2,4-triazole shown in Table 3; 9% by weight of hydrogen peroxide; and water as the balance; the ratio of each of these being a ratio thereof to the total amount.

The resultant polishing slurries for metal were each used to perform etching and CMP polishing and then make evaluation in

the same way as in Example 1. Table 3 shows each etching speed together.

(Table 1)

	Amino-triazole	Metal inhibitor	Copper (unit: nm/minute)	
			Polishing speed	Etching speed
Example 1	3-amino-1,2,4-triazole	benzotriazole	173.4	0.27
Example 2	3-amino-1,2,4-triazole	2-butyl imidazole benzotriazole	221.9	0.46
Example 3	3-amino-1,2,4-triazole	2-ethyl-4-methylimidazole benzotriazole	188.4	0.20
Example 4	3-amino-1,2,4-triazole	2,4-dimethyl imidazole benzotriazole	133.0	0.19
Reference Example 1	3-amino-1,2,4-triazole	None	132.2	2.50
Comparative Example 1	None	None	123.0	4.70

(Table 2)

	Amino-triazole	Metal inhibitor	Tungsten (unit: nm/minute)	
			Polishing speed	Etching speed
Example 6	3-amino-1,2,4-triazole	2-butyl imidazole	120.2	0.33
Example 7	3-amino-1,2,4-triazole	2-butyl imidazole benzotriazole	80.7	0.16
Example 8	3-amino-1,2,4-triazole	2-ethyl imidazole	116.0	1.21
Example 9	3-amino-1,2,4-triazole	2-(isopropyl) imidazole benzotriazole	163.0	1.24
Example 10	3-amino-1,2,4-triazole	2-propyl imidazole benzotriazole	147.0	1.51
Example 11	3-amino-1,2,4-triazole	2,4-dimethyl imidazole benzotriazole	81.0	0.37
Reference Example 2	3-amino-1,2,4-triazole	None	82.2	2.00
Comparative Example 2	None	None	30.2	2.53

(Table 3)

	Metal inhibitor	Etching speed (nm/minute)	
		Copper	Tungsten
Example 13	2-methyl imidazole benzotriazole	0.30	1.00
Example 14	2-ethyl imidazole benzotriazole	0.03	1.21
Example 15	2-(isopropyl) imidazole benzotriazole	0.19	1.24
Example 16	2-propyl imidazole benzotriazole	0.13	1.51
Example 17	2-butyl imidazole benzotriazole	0.46	0.16
Example 18	4-methyl imidazole benzotriazole	0.09	0.15
Example 19	2,4-dimethy limidazole benzotriazole	0.19	0.37
Example 20	2-ethyl-4-methyl imidazole benzotriazole	0.20	0.86
Reference Example 3	2-butyl imidazole	1.80	0.33
Reference Example 4	4-methyl imidazole	2.12	1.40
Reference Example 5	2,4-dimethyl imidazole	1.69	0.36
Reference Example 6	3-amino-1,2,4-triazole	2.50	2.00
Comparative Example 3	benzotriazole	2.50	10.00

In each of Examples 1 to 4, Reference Example 1, the speed of polishing copper was 130 nm/minute or more, and was better than in Comparative Example 1. The etching speed was also a sufficiently lower than in the Comparative Example.

In each of Examples 6 to11, Reference Example 2, the speed of polishing tungsten was 80 nm/minute or more, and was better than in Comparative Example 2. The etching speed was also a sufficiently lower than in the Comparative Example.

In each of Examples 13 to 20, the speed of etching copper was 0.5 nm/minute or less, and was much better than in Comparative Example 3. About tungsten also, the etching speed was a sufficiently lower than in the Comparative Example. In each of Reference Examples 3 to 6, the etching speed was sufficiently lower about tungsten, and was at a practical level.

In each of Examples 13 to 20, Reference Examples 3 to 6, the speed of polishing copper and that of polishing tungsten were 100 nm/minute or more and 20 nm/minute or more, respectively, and were at a sufficiently practical level.

[Example 25]

A polishing slurry for metal was prepared by mixing: 0.15% by weight of malic acid; 0.15% by weight of a water-soluble polymer (an acrylic polymer, weight-average molecular weight: about 10000); 0.3% by weight of 3-amino-1,2,4-triazole; 0.14% by weight of benzotriazole; 0.05% by weight of 2,4-dimethylimidazole; 0.4% by weight of an abrasive (colloidal silica, primary particle diameter: 30 nm); 9% by weight of hydrogen peroxide; and water as the balance.

Trenches of 0.5 to 100 μm depth were made in silicon dioxide, and a tungsten layer of 50 nm thickness was formed as a barrier layer by a known method. A copper film was formed thereon so as to have a thickness of 1.0 μm. A silicon substrate was thus prepared. The substrate was polished with the above-mentioned polishing slurry under the same conditions as in Example 1 until convex portions of the silicon dioxide were exposed in the entire surface of the substrate. The time for the polishing was 2 minutes, and a polishing speed of about 500 nm/minute or more was obtained.

Next, a tracer type level meter was used to obtain the decreased amount of the film thickness of the wiring metal regions with respect to that of the insulating film regions, from the surface shape of a stripe-form pattern wherein wiring metal regions 100 μm in width and insulating film regions 100 μm in width were alternately arranged. As a result, the amount was 70 nm, and was a sufficiently practical value.